Request for Economic Stimulus Funds

<u>Concept</u> <u>Proposal</u>

1. Submitters (Name of Workgroup & Chair/Co-Chairs):
Energy and Sustainability Group (Dr. Doug Whitlock and Dr. James Tracy)

2. Project Title:
One Step Bio-diesel Production via Catalytic-assisting and in-site coupling of Bio-oil Transesterification and Synthesis Gas Supercritical Methanol Synthesis

3. Project Partners (Known or Anticipated):
Western Kentucky University and Eastern Kentucky University

4. Project Background & Purpose (Justification for Project):

The overall goal of this program is to demonstrate the feasibility of in-site coupling concept on bio-diesel production directly using both bio-oil fractions of biomass and various cellulose fractions of biomass.

The transportation sector heavily and almost exclusively relies on petroleum oil as energy source. However, its negative environmental consequences, soaring prices, increasing utilization and competitive supplies have driven dramatic interests in **producing alternative transportation fuels**, which currently include electricity-based, hydrogen-based and biomass-based fuels. Use of either of electricity-based or hydrogen-based alternative energy in the transportation sector is laden with their limited energy densities (175 Wh/kg for battery and 1.32 kWh/liter for H_2, compared to 8.88 kWh/liter for gasoline). **Furthermore, the convenience of using a liquid hydrocarbon fuel through the existing infrastructure has significant advantages over batteries or Hydrogen.** Cellulosic-biomass-derived ethanol and bio-diesel are two promising and predominant alternative renewable transportation liquid fuels, which have comparable energy densities to petroleum-based liquid fuels. Also, it does not compete with human food supplies. A life-cycle evaluation indicated that bio-diesel has advantages over ethanol in both cost and environmental benefits. The combination of gasification and Fischer-Tropsch (F-T) synthesis technologies can convert cellulose-based biomass to bio-fuels, but it is not cost competitive and not flexible enough for implementation at this time. Thus, the question is if there is any economical way to convert total raw material supplies for bio-fuel production, especially bio-diesel. Firstly, cellulose based biomass can be gasified to obtain synthesis gas (a mixture of CO and H_2), which is followed up by being converted into liquid hydrocarbon fuels or oxygenate hydrocarbon fuel through Fischer-Tropsch (F-T) synthesis. Methanol production is regarded to be the most economic starting step in many-year practices of the development of F-T synthesis technology since only C_1 synthesis through F-T process can potentially achieve 100% conversion efficiency. Mobil's F-T synthesis process is based on this understanding. Secondly, the bio-oil part of biomass can be transesterified under available methanol (or mixed alcohols), which can be synthesized in F-T synthesis process using synthesis gas from gasification of cellulose fractions of biomass.

The process analysis of the methanol synthesis process highlights the importance of heat management, thermodynamic shift on one-pass conversion efficiency and synthesis gas stoichiometry. Both the effective in-situ removal of methanol and the economic supply of synthesis gas with the optimized ratio of H_2/CO are likely two major steps to control the large heat transfer duty and further reduce costs for methanol synthesis. The economic index could be further improved if the generated heat in the exothermic methanol synthesis can be taken in-site with coupling other endothermic reactions simultaneously. In an optimal situation, these coupling reactions could be compatible in the in-site integration of both heat transfer and thermodynamic equilibrium shift by methanol removal. **The proposed novel process could realize the economic bio-diesel production by in-site coupling the endothermic transesterification reaction of bio-oil to produce bio-diesel and exothermic methanol synthesis.** The in-site removal of methanol in methanol synthesis could also be realized by consumption of generated methanol by the bio-oil transesterification. To ensure the catalysts are active and to use the heat of reaction effectively, the methanol synthesis process must be operated at temperatures in the range of 200–300 ^{0}C and at pressures in a range of 8-30 MPa. These operational conditions are perfectly compatible to supercritical methanol transesterification of bio-oil. In order to prepare a genuine bio-diesel, it is essential to use methanol prepared from cellulose biomass but not natural gas for bio-diesel production. The raw feedstock for synthesis gas production using co-gasification technologies will be cellulose biomass, together with any byproducts form bio-diesel production process. The adjustability of ideal H_2/CO ratio of synthesis gas could be realized by the co-gasification of cellulose fuel, and tail-gas or any hydrocarbon and oxygenate byproducts from this coupling process of methanol synthesis and bio-oil transesterification.

5. Project Description (General Goals & Implementation Strategies):

The overall goal of this program is to demonstrate the feasibility of in-site coupling concept on bio-diesel production using both bio-boil fractions of biomass and synthesis gas from various cellulose fractions of biomass. The specific goal of the proposed process in Phase I will focus on the demonstration of the feasibility of in-site coupling concept on one-step methanol synthesis and bio-oil transesterification under catalytic assisting supercritical methanol conditions. We aim to optimize the compatibility of these two reactions within one reactor to achieve in-site reaction heat transfer, thermodynamics equilibrium shift, improved reaction conversion kinetics and yields. We will also investigate some possibly unexpected reactions, such as carbon deposit and any poisonous effect of any materials from transesterification of bio-oil on methanol synthesis catalyst. The specific objectives in the pursuit of this goal in Phase I will focus on:

■ To establish guidelines for the selection and evaluation of suitable methanol synthesis catalyst and investigation of its performance (reaction kinetics, conversion yields and catalyst deactivation and interaction with available occurrence of bio-oil transesterification);

■ To establish guidelines for the selection and evaluation of suitable bio-oil transesterification heterogeneous catalyst and investigation of its performance under supercritical methanol conditions (reaction kinetics, conversion yields and catalyst deactivation);

■ To characterization physical properties, quality and purity of the produced bio-diesel;

■ To understand mechanisms on reaction coupling and phase transition of two reactions including methanol synthesis and bio-oil transesterification;

■ To obtain the basic parameters and information for calculation of mass and energy balances of in-site coupling process. Based on obtained information, to primarily estimate benefits gain via coupling concept;

■ To establish a theoretical frame of reaction enthalpy, chemical equilibrium and chemical reaction kinetics for two reactions including methanol synthesis and bio-oil transesterification;

■ To demonstrate the proposed concept in a lab-scale demonstration facility;

■ To find out technical approaches for solving technical problems involved in the in-site coupling reactions, such as carbon deposit on catalyst, interaction between two groups of catalysts and multiply feedstock, immediate and final products, as well as recognition and characterization of any catalyst materials released into bio-diesel;

Phase II will focus on process integration and demonstration.

6. Project Team (Project Manager(s), Content Experts, Instructional Designers, etc.):
Dr. Wei-Ping Pan (Energy balance), Director of Institute for Combustion Science and Environmental Technology
Dr. Yan Cao (Gasification), Assistant Director of Institute for Combustion Science and Environmental Technology
Dr. Chin-Min Cheng (Environmental Engineering), Manager of ICSET
Dr. Buchang Shi (Fischer-Tropsch (F-T) synthesis), Department of Chemistry, Eastern Kentucky University

7. Project Budget & Amount of Economic Stimulus Funds Requested:
ICSET will contribute available facilities, instrument and lab space as primary sources to develop the proposed process, except a few facilities which need to be newly setup. Major funding will be used to support high-quality team to conduct research and development on the proposed concept and process integration. In Phase I, the estimated cost is $800,000 which including (1) Team's salaries and fringes: PI, CO-PI, research Associates, Technicians and Specialists; **total of 8 people**; (2) Newly setup facilities include high-pressure coupling reactor and its accessories; (3) Materials for proposed tests (catalyst, gas and chemicals). In Phase II, the estimated cost is $450,000 for process integration and demonstration. The total cost of this project is **$1,250,000**. Economic Impact: The scientists at the WKU Institute for Combustion Science and Environmental Technology and EKU Department of Chemistry are disclosing through this proposal that they appear to have discovered a new and potentially valuable incremental advantage to the bio-diesel production process. If funded, the results from this project could be an essential element in order to complete the development a truly cost-effective, non-feed stock, bio-diesel production process. If so, the downstream economic and environmental impact from this project could be monumental.